Perfect Layers: a novel class of waterborne resins for 2 component polyurethane coatings

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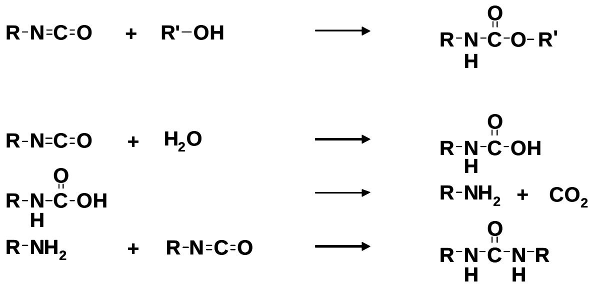
Summary

A novel class of waterborne polyols for 2 component polyurethane coatings has been developed. NOVOS (NO Volatile Organic Solvents) polymers are co-solvent free and combine freedom of (co-solvent) formulation with excellent performance and appearance characteristics. Both the concentration and the type of co-solvent can have a profound effect on film properties in waterborne paints. By using specially designed solvent free secondary polyol emulsions, the so called NOVOS emulsions, the effect of various co-solvent types and concentrations on the film performance of waterborne 2 component polyurethane coatings could be determined. Especially the evaporation rate of co-solvents has a strong effect on properties such as drying time, chemical resistance, König hardness, potlife and blister free film thickness. Because of the nature by which the NOVOS emulsions are prepared, the concentration of acid rich polymer chains is much reduced. This causes the resulting binders to have a significantly improved blister free film thickness (BFFT) compared to traditional secondary emulsions.

Introduction

Today, the latest generations of waterborne 2 component polyurethane coatings can compete with their solventborne counterparts from coating performance perspective: gloss, resistances, durability and hardness are on comparable level. However, the waterborne 2 component polyurethanes do, by nature, exhibit some fundamental differences compared to solventborne. As a result, the application robustness of waterborne systems still shows room for improvement compared to solventborne. The growth of waterborne 2 component systems has therefore been most significant so far within industrial markets where application and drying conditions (temperature, relative humidity) can be controlled.

Firstly, in solventborne coatings polymer and crosslinker are both soluble in the solvent of choice. In waterborne coatings, however, polymer and crosslinker have to be emulsified in water. Especially in the case of the crosslinker this can lead to serious issues [1]. When hydrophobic crosslinkers are selected, high shear needs to be applied for emulsification to prevent inferior film properties [2]. Very often, the hydrophobic crosslinker is dissolved in co-solvents prior to addition to the binder to improve miscibility. An alternative is using hydrophilically modified polyisocyanates. This approach, however, does not always result in the required chemical resistance.



$$R{-}N{=}C{=}O \quad + \quad R'{-}OH \longrightarrow R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R' \qquad (I)$$

$$\begin{aligned} &R{-}N{=}C{=}O \quad + \quad H_2O \longrightarrow R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}OH \\ &R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}OH \longrightarrow R{-}NH_2 \quad + \quad CO_2 \qquad (II) \\ &R{-}NH_2 \quad + \quad R{-}N{=}C{=}O \longrightarrow R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{N}{-}R \end{aligned}$$

Figure 1: The desired reaction in 2 component polyisocyanate curing coatings (I) and reactions occurring upon hydrolysis of the polyisocyanate (II).

Secondly, while in solventborne coatings the solvent is chosen to be inert to the crosslinker, the isocyanate group can readily hydrolyse in waterborne coatings (see Figure 1). Even though in general the rate constants of the reaction between aliphatic polyisocyanates and water are lower than with primary alcohols [3], the excess of water compared to polymer bound hydroxyl groups can cause significant hydrolysis.

The disadvantage of polyisocyanates hydrolyzing is twofold. When an isocyanate group reacts with water an unstable carbamic acid group is formed, which readily dissociates to form an amine group and carbon dioxide. The amine group will subsequently react with a second isocyanate group to form a urea bond (see Figure 1). Hence, hydrolysis does lead to crosslinking, but at the expense of a second crosslinking group. For this reason waterborne 2 component polyisocyanate crosslinking coatings are always formulated at an excess of isocyanate compared to hydroxyl groups. The carbon dioxide formed is an issue especially in thick films. At a dry film thickness of over 50 µm blisters may be formed that affect both aesthetics and coherence of the film, often caused by a combination of air entrapment and carbon dioxide formation.

Acrylic polyol emulsions for 2 component polyisocyanate crosslinking can be prepared according to two processes.

So called primary emulsions are prepared via emulsion polymerization. An advantage of primary emulsions is that particles are formed *in situ* so that no emulsification step is required. Because primary emulsions can have high molecular weights, physical drying times are generally short. A disadvantage of primary emulsions is that film appearance is not always perfect, due to inferior flow and leveling.

Secondary emulsions are made through a process in which the polymer is first polymerized via solution polymerization in an organic solvent. In a next step the polymer solution is emulsified in water after neutralisation of the polymeric acid groups with a base. In the solution polymerization step, good processing is dependent on maintaining low viscosity of the polymer solution. Hence, the polymer is limited in molecular weight or high concentrations of organic solvents need to be used. Since the latter is highly undesired, the molecular weight is generally limited to approximately 50 kg/mole. An advantage of the polymerization in organic solvents is a more homogeneous incorporation of functional groups, such as hydroxyl or acid groups.

Since molecular weights of secondary emulsions are generally lower than those of primary emulsions and relatively high concentrations of organic solvents are used, film appearance of secondary acrylic polyol emulsions crosslinked with polyisocyanates is very good. Significantly higher gloss levels and better DOI are achieved than with primary emulsions. The low molecular weights also result in downsides. Firstly, tack free times are generally much longer than those found for primary emulsions. Secondly, higher hydroxyl concentrations are required to yield the same crosslinking density compared to higher molecular weight resins. Finally, because of the nature of the process by which secondary emulsions are made, they previously always contained organic solvents. This greatly influenced the freedom of the paint formulator in selecting both the optimal solvents and total VOC levels.

In this paper, we describe the effect of co-solvents in waterborne 2 component polyisocyanate curing binders on various film properties. In order to achieve this secondary emulsions were prepared that are essentially free of any solvent.

Results and discussion

Waterborne 2 component polyisocyanate curing binders based on secondary emulsions often contain coalescents. These solvents are chosen because their high boiling points enable effective solution polymerization to high conversion. The disadvantage, however, is that because of the same high boiling point, the evaporation rate in drying films is very slow. In Figure 2 the solvent concentration in 2 component polyisocyanate curing films is pictured as a function of time for the combination of butyl glycol and Solvesso 100. It is clear that the solvents disappear only slowly. After 24 hours less than 80 % of the coalescents had evaporated.

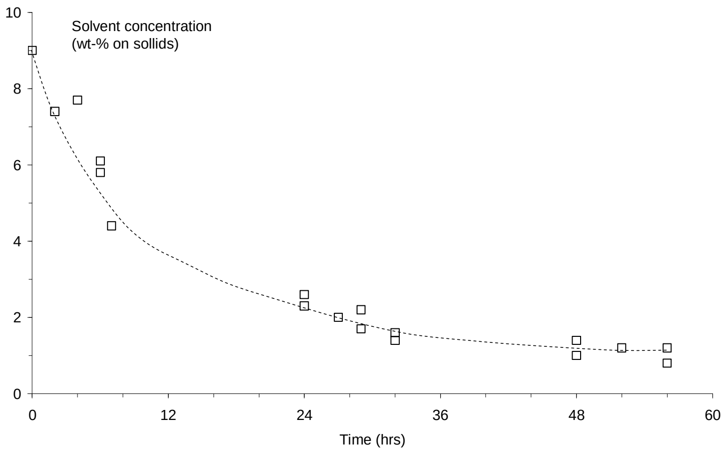


Figure 2: Solvent concentration as a function of time in a 2 component polyisocyanate curing film. Starting concentration was 9 wt-% of a 50/50 mixture of butyl glycol and Solvesso 100.

Striving towards a more sustainable world, we intend to minimize the use of co-solvents in waterborne paints. The choice of quality of the coalescent for the application of choice is, however, also very relevant. For waterborne 2 component polyisocyanate crosslinking coatings this topic has been discussed only to a limited extent [3,4]. The main point of discussion in these papers has been the use of protic coalescents. The comments were that the use of isocyanate reactive solvents does not appear to affect film performance negatively.

We investigated the effects of a series of co-solvents (see Table 1), with various evaporation rates and different degrees of solubility in water, in 2 component polyisocyanate curable binders whereby new solvent-free waterborne polyol emulsions were used. These so called NOVOS emulsions have the advantage of allowing selection of the optimal coalescent in terms of film performance and give the formulator increased flexibility of achieving the desired VOC level.

Table 1

Evaporation rate and water solubility of coalescents

	Evaporation rate (BuAc = 100)	Water solubility (%)
Dowanol PM	66	100
Dowanol MPA	34	18
Dowanol DMM	16	50
Butyl glycol	6	100
Dowanol DPM	2	100
Butyl diglycol	0.3	100
Solvesso 100	19	< 0.01

In all cases an overall coalescent concentration of 8 wt-% on total emulsion was used. For the purpose of comparison, secondary emulsions were used based on three different polymer compositions, having OH concentrations of 3.3 %, 4.2 %, and of 5.0 % (corresponding with OH numbers of 108.9, 138.6, and 165.0 mg KOH/g of solid resin, respectively).

In Tables 2, 3 and 4 overviews are given of application properties for the most relevant coalescents for the three different emulsions. The results compare as expected. With increasing hydroxyl number chemical resistances and König hardness increased. Due to the higher concentration of polyisocyanate in these films tack free times increased as well.

Table 2
Effect of co-solvent type on final film properties for the secondary emulsion having an OH concentration of 3.3 % formulated with an NCO:OH ratio of 1.2.

	Dowanol PM	Dowanol MPA	Dowanol DMM	Butyl glycol	Dowanol DPM	Butyl diglycol	Solvent free	Reference combination[i]
Gloss (20/60)	55/86	40/87	41/81	62/89	71/92	28/70	71/93	75/94
Appearance	OK	OK	Grains	OK	OK	Flat	Ok	OK
DFT[ii] (min)	10	10	10	15	25	120	10	15
TFT[iii] (min)	35	35	60	75	120	330	75	120
Hardness[iv] (s)	140	133	115	132	102	80	151	140
MEK [dr][v]	170	180	180	130	130	90	220	160
Adhesion to CRS	2	1	1	1	1	1	1	1
BFFT[vi] (µm)	100	100	100	Sediment	100	Sediment	100	100

i: The reference emulsion contains a 50/50 mixture of butyl glycol and Solvesso 100, *ii*: dust free time; *iii*: tack free time; *iv*: König hardness after 24 hrs; *v*: MEK double rubs; *vi*: blister free film thickness above which CO_2 blisters are visible.

Table 3
Effect of co-solvent type on final film properties for the secondary emulsion having an OH concentration of 4.2 % formulated with an NCO:OH ratio of 1.2.

	Dowanol PM	Dowanol MPA	Dowanol DMM	Butyl glycol	Dowanol DPM	Butyl diglycol	Solvent free	Reference combination
Gloss (20/60)	78/91	74/91	73/90	77/91	69/90	65/87	72/90	77/90
Appearance	OK	OK	Grains	Grains	OK	Grains	OK	OK
DFT[ii] (min)	15	20	60	30	60	210	30	30
TFT[iii] (min)	165	195	180	180	210	> 360	180	210
Hardness[iv] (s)	154	153	144	147	129	88	153	155
MEK [dr][v]	> 200	> 200	> 200	> 200	> 200	200	> 200	> 200
Adhesion to CRS	2	0	1	2	2	1	2	2
BFFT[vi] (µm)	> 100	100	100	100	> 100	90	100	90

i: The reference emulsion contains a 50/50 mixture of butyl glycol and Solvesso 100, *ii*: dust free time; *iii*: tack free time; *iv*: König hardness after 24 hrs; *v*: MEK double rubs; *vi*: blister free film thickness above which CO_2 blisters are visible.

Table 4
Effect of co-solvent type on final film properties for the secondary emulsion having an OH concentration of 5.0 % formulated with an NCO:OH ratio of 1.2.

	Dowanol PM	Dowanol MPA	Dowanol DMM	Butyl glycol	Dowanol DPM	Butyl diglycol	Solvent free	Reference combination[i]
Gloss (20/60)	30/73	73/90	67/89	42/82	39/70	14/45	74/90	77/90
Appearance	Haze	OK	OK	Haze	Haze	Haze	OK	OK
DFT[ii] (min)	10	10	25	10	45	120	10	20
TFT[iii] (min)	150	150	165	165	225	> 360	150	150
Hardness[iv] (s)	185	189	183	181	180	160	189	186
MEK [dr][v]	1000	1000	750	700	1000	425	1000	900
Adhesion to CRS	2	2	2	2	3	1	4	3
BFFT[vi] (µm)	90	100	90	Gelled	100	> 100	90	90

i: The reference emulsion contains a 50/50 mixture of butyl glycol and Solvesso 100, *ii*: dust free time; *iii*: tack free time; *iv*: König hardness after 24 hrs; *v*: MEK double rubs; *vi*: blister free film thickness above which CO_2 blisters are visible.

For all secondary emulsions an increase in drying times was observed with decreasing rate of evaporation of the coalescent. This makes sense. Films comprising the solvents with slow evaporation rates also yielded significantly softer films. This could be explained by solvent retention in the drying film. What is surprising though is that using solvents with a high evaporation rate yielded tack free times that could even be shorter than that of the solvent free systems. This is further illustrated in Figure 3 for the polyol with an OH number of 3.3 %. In the first 30 minutes of film formation, the rate of evaporation was significantly increased when using Dowanol MPA compared to the film comprising the slower evaporating Solvesso 100. The weight loss of the film cast without any co-solvents ran nicely between those of the slow and fast solvent. Hence, the choice of solvents clearly affects the evaporation from the film which, in turn, affects drying properties.

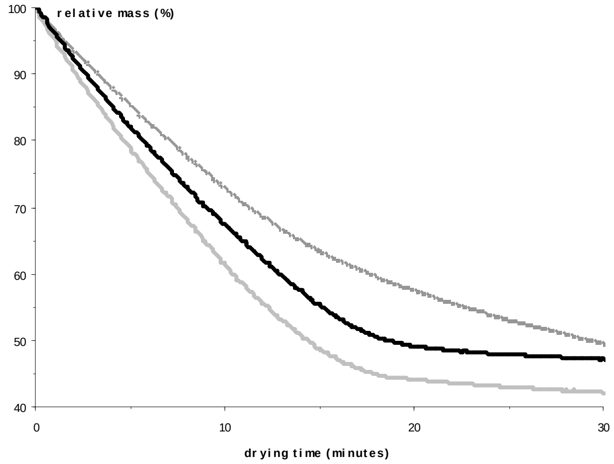


Figure 3: Weight loss of drying films of polyols with a hydroxyl number of 3.3 %, formulated at an NCO:OH ratio of 1.2. The black line represents the film not containing co-solvents, the upper grey line represents the film containing Solvesso 100, the lower grey line represents the film containing Dowanol MPA. The films were dried at a temperature of 23 °C and a relative humidity of 50 %.

Only when using the extremely slowly evaporating butyl digycol, or to a lesser extent Dowanol DPM, a significant decrease in chemical resistances and surface hardness compared to the faster evaporating coalescents was observed. The main reason for this is most likely co-solvent retention in the film. This can also be observed when looking at the development of viscosity of the drying films. With decreasing evaporation rate of the solvent, not only a slower built-up of the film viscosity was observed, also the final film viscosity was reduced. This can be seen in figures 4 and 5, where development of film viscosity during the first stages of film formation is shown as a function of time.

In the absence of polyisocyanate crosslinker the choice for Dowanol PM or BDG resulted in a difference of 2 decades in film viscosity as observed after 60 minutes of film formation. The viscosity of the film containing Dowanol PM reached such high values within 60 minutes that the viscosity could no longer be measured. When films containing Dowanol PM formulated with and without isocyanate are compared (figures 4 and 5), it can be seen that the viscosity development for the isocyanate free film was faster. This can be explained by the crosslink kinetics, since during the initial stage of the film formation hardly any crosslinking took place (as could be confirmed with infrared measurements), leaving the free isocyanate as a plasticizer. For BDG this effect was less pronounced.

The difference in viscosity of the drying films containing crosslinker after 3 hours of film formation between films cast from emulsions containing Dowanol PM or Dowanol DPnB was almost one decade. This is in line with the very short tack free times of solvent free films. The formulation without solvent was even faster. Hence, although the viscosities of the drying films reflect the effect the rate of evaporation of the solvents, they do not explain why formulations comprising fast evaporating solvents yielded shorter tack free times than the NOVOS emulsion.

The differences in viscosity after film formation suggest that perhaps not all solvent evaporated and films comprising the slower evaporating solvents suffered from solvent retention more significantly than the films with faster evaporating solvents. This also explains the differences in viscosity build up for the films with and without crosslinker. In the presence of BDG the free isocyanate will not reduce the viscosity significantly, but in the case of Dowanol PM the solvent will no longer be present, leaving only the isocyanate as plasticizer. Much in line with the plot shown in Figure 2, this was confirmed for films comprising Dowanol PM or Solvesso 100. After ageing for 48 hours at room temperature these films still contained 0.63 % and 1.5 % of solvent, respectively. Solvesso 100, being the slower evaporating solvent, showed more retention, which is consistent with the lower viscosity of this film as shown in Figure 5. The high value for Dowanol PM, corresponding to more than 12 % of the concentration that was originally added, however, was surprisingly high. This too, however, was consistent with the reduced film viscosity compared to that of the solvent free film.

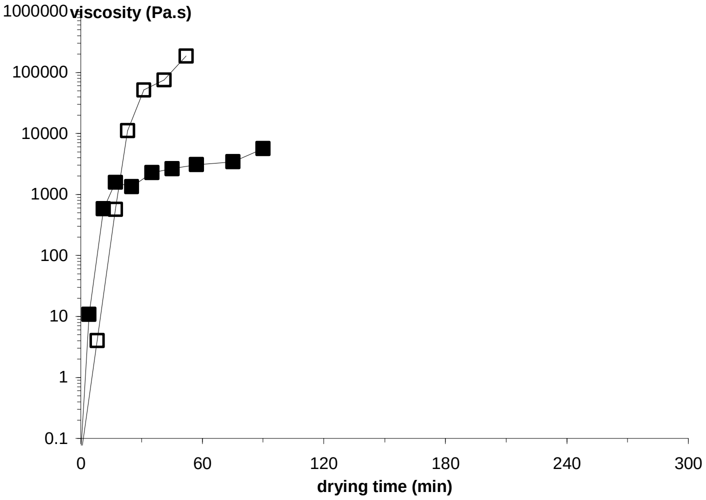


Figure 4: Viscosity as a function of time for films cast from the emulsion with a hydroxyl content of 4.3 % in the absence of crosslinker, formulated with different coalescents. The curves represent the films formulated with BDG (■) and Dowanol PM (□).

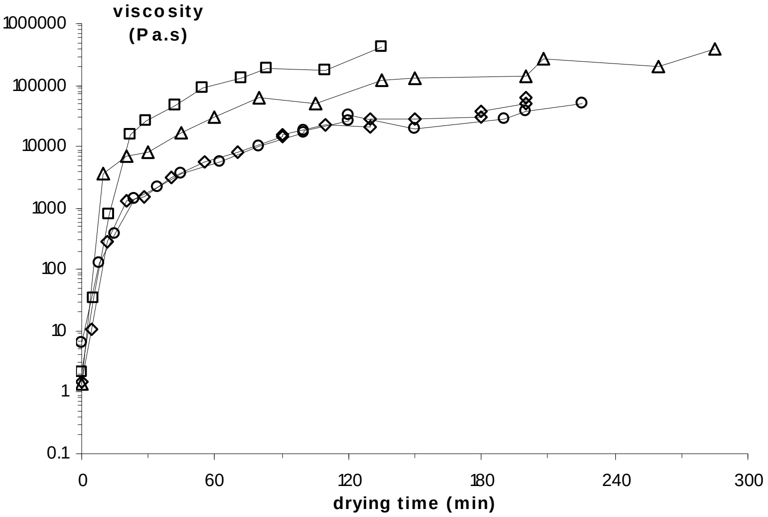


Figure 5: Viscosity as a function of time for films cast from the emulsion with a hydroxyl content of 4.2 % formulated with different coalescents. The curves represent the solvent free film ('), Dowanol PM (+), BDG (() and Dowanol DPnB ()).

The use of protic solvents led to sediment formation, grains, hazy films or even gellation. Hence, formulating these types of binders with, for instance, butyl glycol or butyl glycol is not preferred.

These results seem to be in contrast with results reported in literature [4]. When the hydroxyl number was increased to 4.2 % or even 5 %, however, no stability problems were observed. Apparently, the higher hydroxyl numbers provide sufficient additional stabilisation to prevent settlement. These films did, however, still yield films with grains or a haze.

The choice of solvent was also found to affect pot life of 2 component polyurethanes based on acrylic polyol emulsions. In Table 5 the initial 20 ° gloss values are compared with the gloss levels measured after a pot life of 2 hours and 4 hours.

Table 5
Gloss levels as a function of pot life of waterborne 2 component polyurethanes based on emulsions with a hydroxyl content of 4.2 % (formulated with different coalescents).

Coalescent	20 ° gloss		
	t = 0 hrs	t = 2 hrs	t = 4 hrs
Dowanol PM	78	76	78
Dowanol MPA	82	77	70
Dowanol DPM	77	66	60
Solvesso 100	85	84	82
solvent free	84	84	82

Compared to the solvent containing emulsions, the NOVOS emulsion clearly yielded very good gloss retention, indicative for a prolonged pot life. Comparing the effects of the coalescents, gloss retention improved with increasing evaporation rate. Although it can be argued that a slowly evaporating solvent would be beneficial for extension of pot life because it will plasticise pre-crosslinked material. This statement can, however, not be supported by these data.

Having established how effective the proper selection of solvents is, the effect of solvent concentration was investigated too. For this purpose we selected a very fast coalescent, Dowanol MPA, and a very slow coalescent, butyl diglycol. In Tables 6 and 7 the film properties of emulsions formulated with concentrations varying between 1 and 12 % are shown for these coalescents.

Table 6
Effect of Dowanol MPA concentration on final film properties for the secondary emulsion having an OH concentration of 4.2 % formulated with an NCO:OH ratio of 1.2.

FAST	Solvent concentration					
	0 %	1 %	2 %	4 %	8 %	12 %
Gloss (20°/60°)	81/92	80/91	80/92	79/91	81/92	80/91
DFT [i] (min)	15	20	20	20	20	20
TFT [ii] (min)	150	150	150	150	150	150
König hardness						
after 1 day	185	172	172	172	172	172
after 4 wks	202	204	204	203	204	202
MEK [iii] [dr]	375	315	240	270	270	325

i: dust free time; *ii*: tack free time; *iii*: MEK double rubs;

Table 7
Effect of butyl diglycol concentration on final film properties for the secondary emulsion having an OH concentration of 4.2 % formulated with an NCO:OH ratio of 1.2.

SLOW	Solvent concentration					
	0 %	1 %	2 %	4 %	8 %	12 %
Gloss (20°/60°)	80/93	83/93	83/94	83/92	83/92	81/91
DFT [i] (min)	15	15	30	60	135	240
TFT [ii] (min)	150	150	180	255	360	> 360
König hardness						
after 1 day	185	175	162	123	95	80
after 4 wks	202	196	180	168	154	147
MEK [iii] [dr]	375	365	280	215	160	115

i: dust free time; *ii*: tack free time; *iii*: MEK double rubs;

For the fast evaporating Dowanol MPA hardly any effect of the solvent concentration was observed except that slightly better chemical resistance, initial hardness and shorter dust free time were found for the complete co-solvent free formulation. In view of the fast evaporation of the solvent as well as the accelerating effect MPA has on the evaporation of water, this is not a surprising result. In Table 7, however, it can be seen that a strong effect of the butyl diglycol concentration (slow solvent) was observed on especially tack free time, König hardness and MEK resistance. Just as discussed for the data presented in Tables 2, 3, and 4, retention of butyl diglycol in the drying film is likely to have a very negative effect on these properties. Comparing the data for high butyl diglycol concentrations with the lower values, however, teaches that already at low concentrations smooth and coherent films are formed, with high gloss readings. Hence, high concentrations of butyl diglycol are not required for good film formation. This means that the concentration of coalescent can also be used to tailor the desired film properties, such as for instance drying time.

When comparing coalescents with different solubility in water no clear effects were observed. For the two emulsions with the lower hydroxyl number, the reference coalescent combination yielded significantly longer tack free times than when only butyl glycol was used. This could lead to the conclusion that decreased water solubility of the coalescent does indeed lead to longer drying times.

Film formation of the solvent free polyol emulsions was good as was concluded from the high gloss readings in Tables 2, 3 and 4. The extent of film formation was further investigated using AFM. In Figure 6 the topology pictures of polyol emulsions formulated with the standard solvent combination (being 4 wt-% of Solvesso 100 and 4 wt-% of butyl glycol) was compared to that of the solvent free film. As can be seen film formation was perfect in both cases. This can also be judged from the height differences in the z-range, which was 11 nm for both films.
Hence, also from a microscopical view point film formation in the absence of co-solvents is as good as when using powerful coalescents.

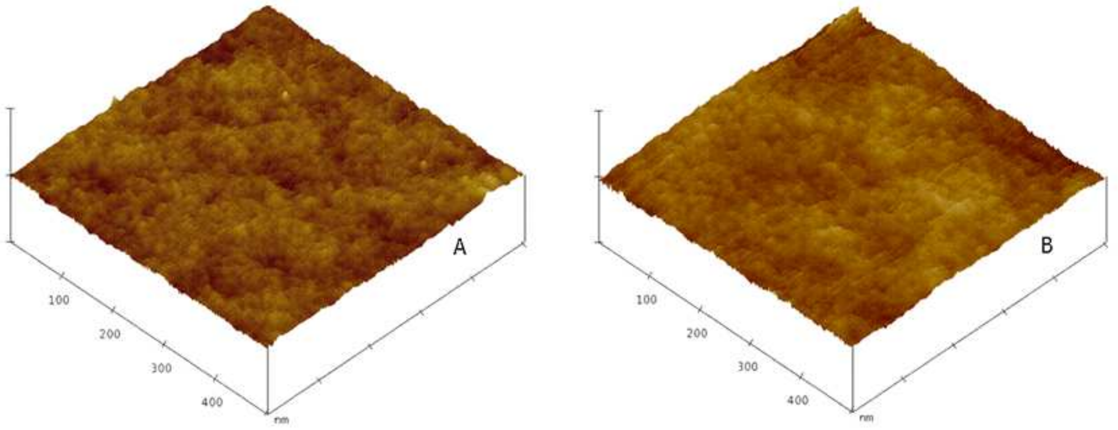


Figure 6: Profile plots of solvent containing (A) and solvent free (B) 2 component polyisocyanate cured films.

Overall, it can be concluded that for waterborne 2 component polyisocyanate crosslinking coatings proper co-solvents need to be carefully selected. For particular application purposes properties such as drying times, gloss values or chemical resistances may need to be tailored. This can be readily achieved by selecting the proper solvent or mixture of solvents.

Solvent free, zero VOC secondary emulsions on themselves can already provide an interesting set of film properties. Especially gloss, König hardness, and chemical resistances were at a very high level. However, also the pot life is influenced by the choice of solvent.

In all cases (co-solvent free as well as for all additional solvent types) surprisingly high BFFT (Blister Free Film Thickness) values were observed. Using gradient HPLC the chemical composition distribution of polyols prepared according to the new NOVOS process was compared with that of the traditional solvent assisted dispersions, before and after methylation of the acid groups. The principle difference between the former and the new process in terms of chemical composition distribution was found to be that the new process resulting in the NOVOS-emulsions yields far less low molecular weight, acid rich material. In previous papers the role of acid rich material in the formation of carbon dioxide blisters was discussed [5]. High concentrations of polymer chains with a high acid load will result in a higher concentration of water in the drying film. This water causes more extensive hydrolysis of polyisocyanates during cure, which in turn results in the formation of blisters. Hence, when the new polymerization process is followed less acid rich polymer chains are being formed, finally resulting in reduced in an improved blister free film thickness.

Conclusions

A new class of secondary polyol emulsions for 2 component polyurethane coatings has been developed. These so called NOVOS emulsions yield a very interesting set of film properties. Compared to the traditional solvent containing secondary emulsions chemical resistances and drying times are much improved. A distinct advantage of the NOVOS emulsions is their significantly higher blister free film thickness (BFFT) of more than 100 µm.

An additional advantage of the solvent free polyol emulsions is that they provide the formulator flexibility in choice and concentration of coalescents. Especially the evaporation rate of co-solvents was found to have strong effect on tack free times and König hardness. Solvents with a slow evaporation rate yielded reduced hardness values and also reduced chemical resistance. These effects could be explained by means of rheological measurements, showing a slower built-up of viscosity and a reduced final viscosity when slowly evaporating coalescents were used. For fast evaporating solvents, the tack free time was found to be reduced even compared to solvent free emulsions. Especially for coalescents with a low evaporation rate, the concentration of coalescent was also found to influence film properties such as drying time, without affecting film formation.

Surprisingly, the choice of co-solvent was also found to have an effect on pot life. Improved gloss retention as a function of pot life was observed for solvents with a high rate of evaporation.

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